into the equivalent quantity in vacuum and bring their results into much closer agreement with the other entries in Table II.

Registry No. PPCS, 24991-47-7; PPFS, 24936-47-8; PPBS, 24936-50-3; PPMOS, 24936-44-5; PPFαMS, 42475-56-9; PPBαMS, 86068-37-3; PNVC, 25067-59-8.

References and Notes

(1) Volkenstein, M. W. "Configurational Statistics of Polymer Chains"; Interscience: New York, 1963.
(2) Burshtein, T. M.; Ptitsyn, O. B. "Conformation of Macromolecules"; Interscience: New York, 1966.
(3) Flory, P. J. "Statistical Mechanics of Chain Molecules"; Interscience: New York, 1969.
(4) Stockmayer, W. H. *Pure Appl. Chem.* **1967**, *15*, 539.
(5) Mark, J. E. *Acc. Chem. Res.* **1974**, *7*, 218.
(6) Block, H. *Adv. Polym. Sci.* **1979**, *33*, 93.
(7) Kotera, A. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 750.
(8) Burshtein, L. L.; Stepanova, T. P. *Vyoskomol. Soedin., Ser. A* **1969**, *11*, 2885.
(9) Baysal, B.; Lowry, B. A.; Yu, H.; Stockmayer, H. In "Dielectric Properties of Polymers"; Karasz, F. E., Ed.; Plenum Press: New York, 1972.
(10) Roig, A.; Fuentes, I. H. *An. Quim.* **1974**, *70*, 668.
(11) Mashimo, S.; Nozaki, R.; Work, R. N. *J. Chem. Phys.* **1982**, *77*, 2663.
(12) Blasco, F.; Riande, E. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 835.
(13) Tonelli, A. E.; Belfiore, L. A. *Macromolecules* **1983**, *16*, 1740.
(14) Orhan, E. H.; Akovali, G.; Baysal, B. M. *Makromol. Chem.* **1976**, *177*, 3009.
(15) Lenz, R. W.; Westfelt, L. C. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 2147.
(16) Guggenheim, E. A.; Prue, J. E. "Physico-Chemical Calculations"; Interscience: New York, 1955; p 106.
(17) Smith, J. W. "Electric Dipole Moments"; Butterworths: London, **1955**; p 60.
(18) Saiz, E.; Mark, J. E.; Flory, P. J. *Macromolecules* **1977**, *10*, 967.
(19) McClelan, A. L. "Tables of Experimental Dipole Moments"; W. H. Freeman: San Francisco, 1963.
(20) Aroney, M. J.; Calderbank, K. E.; Le Fêvre, R. J.; Pierens, R. K. *J. Chem. Soc. B* **1969**, 159.
(21) Mikhailov, G. P.; Burshtein, L. L.; Andreyeva, T. P. *Vyoskomol. Soedin., Ser. A* **1967**, *9*, 2963.
(22) Masegosa, R. M.; Hernandez-Fuentes, I.; Ojalvo, E. A.; Saiz, E. *Macromolecules* **1979**, *12*, 862.
(23) Kücükyavuz, Z.; Baysal, B. M. *Prep., IUP Symp. Macromolecules, Florence*, Sept 1980, p 466.
(24) Kücükyavuz, Z.; Baysal, B. M., unpublished results.
(25) Chiba, A.; Uzawa, S.-i.; Uda, M.; Doi, S. *Prog. Polym. Phys. Jpn.* **1974**, *17*, 105.
(26) Yamaguchi, N.; Sato, M.; Ogawa, E.; Shima, M. *Polymer* **1981**, *22*, 1464.
(27) Kern, W.; Brawn, D. *Makromol. Chem.* **1958**, *27*, 23. Takashima, K.; Tanaka, G.; Yamakawa, H. *Polym. J. (Tokyo)* **1971**, *2*, 245.
(28) Mohite, R. B.; Fundiah, S.; Kapur, S. L. *Makromol. Chem.* **1968**, *116*, 280.
(29) Mark, J. E. *J. Chem. Phys.* **1972**, *56*, 458.
(30) Yoon, D. Y.; Sundararajan, P. R.; Flory, P. J., *Macromolecules* **1975**, *8*, 776.
(31) Yoshihara, M., Work, R. N.; *J. Chem. Phys.* **1982**, *76*, 5174.
(32) Halverstadt, I. F.; Kumler, W. D. *J. Am. Chem. Soc.* **1942**, *64*, 2988.
(33) Onsager, L. *J. Am. Chem. Soc.* **1936**, *58*, 1486.

Temperature Dependence of Swelling of Polystyrene Networks

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Received December 12, 1984

ABSTRACT: Swelling of polystyrene networks in cyclohexane is measured as a function of temperature in the interval between 16 and 45 °C. The increase of network volume over the stated temperature interval is observed to be three- to fourfold, depending on the degree of cross-linking. Results of swelling in toluene are used to calculate the cross-link density. The expression for the chemical potential of solvent in the network is used to predict the degree of swelling. The interaction parameter required for the formulation is taken from experimental results obtained by previous workers. Satisfactory agreement of experiments with predictions of the theory based on the chemical potential expression confirms the postulate of additivity of the mixing and elastic free energies of swollen networks. Swelling of the networks is also measured in a mixture of toluene and methanol, 75/25 wt %. The experimental technique employed provides a convenient means of comparing the swelling effects of cyclohexane and toluene–methanol, which are both Θ solvents for polystyrene around 35 °C. Results of swelling measurements in the toluene–methanol mixture are used to determine its interaction parameter with polystyrene.

Introduction

The chemical potential of a solvent in a network is expressed as[1]

$$(\mu_1 - \mu_1{}^0)/RT = \ln(1 - v_2) + v_2 + \chi v_2{}^2 + \partial \Delta A_{\mathrm{el}}/\partial n_1 = \ln a_1 \quad (1)$$

where μ_1 and $\mu_1{}^\circ$ are the chemical potentials for the solvent in the presence and absence of the polymer, respectively, v_2 is the volume fraction of polymer in the swollen system, χ is the reduced chemical potential[2] or the so-called χ parameter for the system, and $\partial \Delta A_{\mathrm{el}}/\partial n_1$ represents the elastic contribution obtained as the gradient of the elastic free energy, ΔA_{el}, of the network with respect to the number, n_1, of solvent molecules. a_1 is the solvent activity and R and T are the gas constant and absolute temperature, respectively.

When the network is in thermodynamic equilibrium with the surrounding solvent, the expression given by eq 1 equates to zero. If the elastic contribution and the degree of equilibrium swelling are known, eq 1 may be solved for the χ parameter. Conversely, if the χ parameter and the degree of swelling are known, the elastic contribution may be obtained, from which the degree of cross-linking may be evaluated.

Extensive work has been done over the past years on the thermodynamics of the polystyrene–cyclohexane system[3-7] from which the χ parameter has been evaluated. Light scattering, osmotic and vapor pressure, sedimentation equilibrium, and critical miscibility measurements are among the different methods employed. Results of the several different measurements of the χ parameter of the polystyrene–cyclohexane system are in quantitative agreement, showing strong dependence of this parameter on concentration and temperature.

In this study, linear swelling ratios for polystyrene networks in cyclohexane are measured over a wide temperature range (15–45 °C). Results of swelling measurements are compared with eq 1 in which the previously obtained expressions for the χ parameter are employed. Swelling of the networks in a mixture of toluene–methanol (75/25 wt %) is also investigated, and the χ parameter of this system is estimated by the use of eq 1.

Experimental Section

Preparation of Networks. Inhibitor-free dry styrene was freshly distilled under reduced pressure prior to use. *p*-Divinylbenzene was a Merck material that contained 50% divinylbenzene and 50% ethylvinylbenzene. Its inhibitor was removed. Benzoyl peroxide was recrystallized and dried.

Proper mixtures of styrene, benzoyl peroxide, and *p*-divinylbenzene were placed in clean *pyrex* tubes, degassed three times, and sealed under vacuum. The charged tubes were then transferred to an oven at 60 ± 0.05 °C and polymerized for 66 h.

Two cross-linked polystyrene networks were prepared by using this procedure. Both of these samples contained 10.0 mL of styrene and 0.2424 g (0.001 mol) of benzoyl peroxide. One of the samples, called sample 1 hereafter, contained 0.03 g of divinylbenzene as the cross-linking agent. The other sample, referred to as sample 2, contained 0.02 g of divinylbenzene.

Measurements. Samples with dimensions of ca. 8 × 3 × 1 mm^3 were machined from the dry, glassy cross-linked network. Two pieces of thin wires were placed approximately at a distance of 6 mm in each sample, forming fiducial marks from which linear deformation upon swelling was measured. Samples were stored horizontally in a constant-temperature bath (±0.02 °C), and measurements of length changes were made in the immersed state. This method of measurement is found to be more accurate than gravimetric techniques employed in previous studies. Length changes were measured with an accuracy of ±0.001 cm with a traveling microscope (Gaertner 7109-C-46). At temperatures above 20 °C, complete swelling equilibrium was obtained within 2–3 h following a temperature increase. Final readings were made at least 6 h after each temperature change. Below 20 °C, at least 24 h was allowed for equilibrium. Readings were taken in both the increasing and decreasing directions of temperature and were observed to be reproducible.

Results of Measurements

Results of measurements of swelling of samples with changes in temperature are shown as experimental points in Figures 1 and 2. Best fitting curves through the experimental points are drawn according to the least-squares approximation. Deformations indicated by the linear swelling ratio are represented by the parameter $\lambda = L/L_0$ on the left ordinate, where L is the length of the swollen sample at temperature T and L_0 is the corresponding length of the unswollen network at T = 25 °C. Values of volume fraction, $v_2 = \lambda^{-3}$, are shown on the right ordinate.

In Figure 1, filled circles represent results of measurements for sample 1, and empty circles for sample 2, both in cyclohexane. In Figure 2, the results of swelling of sample 1 in toluene (upper set of filled circles) and in a mixture of toluene–methanol (empty circles) are shown. The ratio of toluene to methanol was 3:1 by weight, which forms a Θ solvent for polystyrene[8] at 34 °C. The lower set of filled circles in Figure 2 represents results for swelling of sample 2 in cyclohexane, reproduced from Figure 1 for comparison.

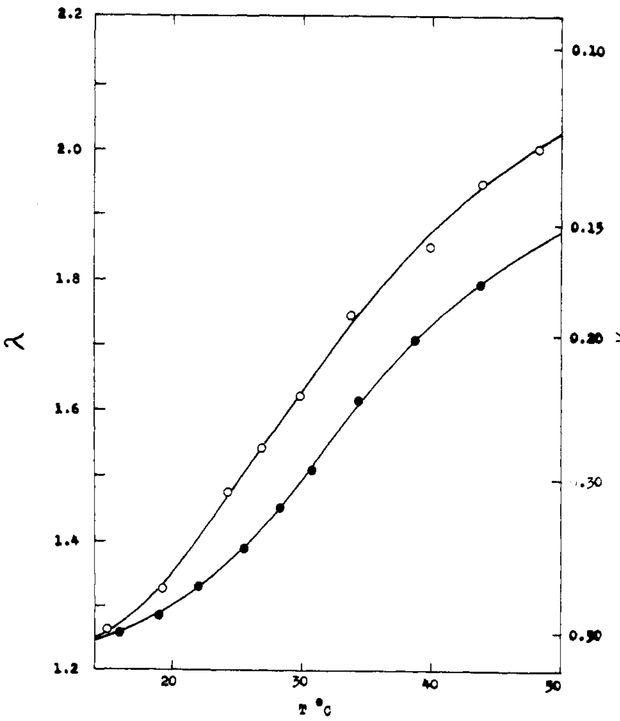

Figure 1. Results of swelling measurements for polystyrene networks in cyclohexane plotted as a function of temperature. Filled circles show results for sample 1, and empty circles for sample 2. Curves through the points are the best fitting curves obtained by least squares. Linear swelling ratio and polymer volume fraction are shown on the left and right ordinates, respectively.

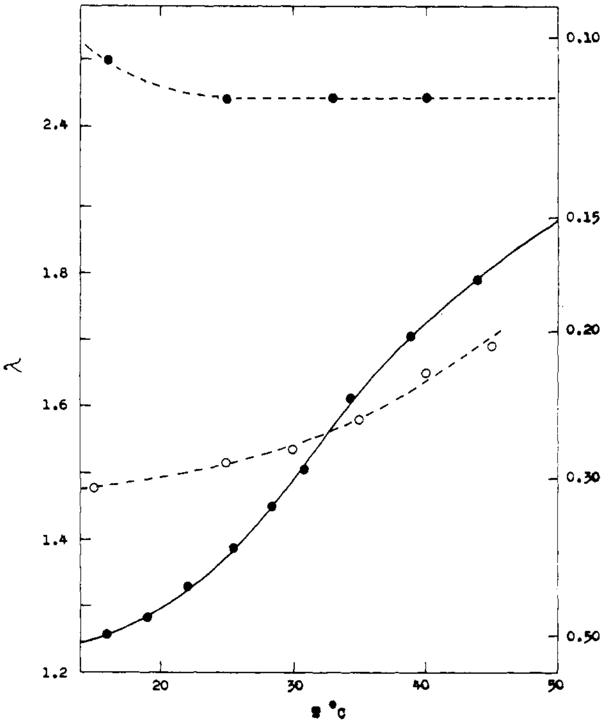

Figure 2. Results of swelling measurements for polystyrene in toluene (upper set of filled circles) and in toluene–methanol (empty circles) plotted as a function of temperature. Data for sample 1 are shown only. Lower set of filled circles is for polystyrene in cyclohexane for sample 1 and is included for comparison. Curves through the points are the best fitting curves by least squares. Linear swelling ratio and polymer volume fraction are shown on the left and right ordinates, respectively.

Comparison of Experimental Results with Theory

Elastic Contribution. The form of the elastic free energy is required both for the estimation of the degree of cross-linking form swelling experiments and for the analysis, in general, of swelling phenomena by using eq 1. Experimental work on the elasticity of amorphous rubbery networks[9] shows that the results may be accurately predicted by the recent theory introduced by Flory.[10] The expression for the contribution, $\partial \Delta A_{el}/\partial n_1$, to the chemical potential of the solvent is obtained according to the theory as

$$\partial \Delta A_{el}/\partial n_1 \equiv (\mu_1 - \mu_1^0)_{el}/RT = (v_1/V^0)\lambda^{-1}[\xi + \mu_j K(\lambda)] \quad (2)$$

where v_1 is the molar volume of the solvent, V^0 is the reference volume, and ξ and μ_j are the cycle rank and the number of junctions, respectively. $K(\lambda)$ follows from the theory as

$$K(\lambda) = B\dot{B}/(1 + B) + D\dot{D}/(1 + D) \quad (3)$$

where

$$B = \kappa^2(\lambda^2 - 1)/(\lambda^2 + \kappa)^2$$

$$D = \lambda^2 B/\kappa$$

$$\dot{B} = \partial^2 B/\partial\lambda^2 = B[(\lambda^2 - 1)^{-1} - 2(\lambda^2 + \kappa)^{-1}]$$

$$\dot{D} = \partial^2 D/\partial\lambda^2 = \kappa^{-1}[\lambda^2\dot{B} + B] \quad (4)$$

Here, κ is a parameter denoting the degree of the effect of constraints on the fluctuations of junctions. $\kappa = 0$ and ∞ correspond respectively to the phantom and the affine network theories.[10] Theory shows that the value of κ is inversely proportional to the square root of the cross-link density,[9] given by the expression

$$\kappa = I(N_A d l^2 C_\infty/2M_l)^{3/2}(kT)^{1/2}(\xi kT/V^0)^{-1/2} \quad (5)$$

where I is a universal constant of proportionality, experimentally obtained as $^1/_2$ for several networks, N_A is Avogadro's number, d is the density, C_∞ is the characteristic ratio, l is the length of a repeat unit, and M_l is its molecular weight. The term $\xi kT/V^0$ represents the modulus of the network that would be obtained in the absence of constraints. Taking $l = 1.53 \times 10^{-8}$ cm, $C_\infty = 8.5$, and $M_l = 50$ for polystyrene, eq 5 reduces to

$$\kappa = 1.334(\xi kT/V^0)^{-1/2} \quad (5')$$

when the numerical coefficient is in units of $N^{1/2}$ mm^{-1}. In a real network κ varies, in general, between 0 and 15, depending on the degree of cross-linking. The dependence of the modulus of a dry rubbery network on deformation may conveniently lead to the value of κ as has been reported previously.[9] Due to difficulties in performing elasticity experiments on dry polystyrene networks in the rubbery state, it was not possible to determine the κ values of the two networks in this manner, however. Instead, values of κ obtained from eq 5′ are used as explained below.

Calculation of the Degree of Cross-Linking. The degree of cross-linking of samples 1 and 2 is obtained by measuring the degree of equilibrium swelling of the networks in toluene. The χ parameter of polystyrene–toluene at 22–30 °C is obtained from the data compiled by Orwoll.[11] The data show that the χ parameter for this system depends on the polymer volume fraction. A linear least-squares analysis gave the relationship

$$\chi = 0.455 - 0.155v_2 \quad (6)$$

Substitution of eq 6 and 2 into eq 1 and using eq 5′ for κ lead to an expression for the solvent chemical potential in terms of v_2 and $\xi kT/V^0$. The value of $\xi kT/V^0$ satisfying $\Delta\mu_1 = 0$ for the experimentally observed value of v_2 at equilibrium swelling may be obtained numerically. The corresponding value of κ is then obtained from eq 5′. Results of swelling measurements in toluene and calculations for the two networks are summarized in Table I. The first column in Table I gives the v_2 value for equilibrium swelling in toluene observed at 25 °C. In the second column values of κ are given. Values of the modulus, $\xi kT/V^0$, obtained by solving eq 1, are shown in column 3. In the fourth column, the modulus values calculated from chemical constitution assuming complete reaction of the divinylbenzene are given. The threefold difference between chemically determined values and those from equilibrium swelling may predominantly be due to wasted divinylbenzene in forming loops, dangling chains, and other imperfections. The value of the cycle rank obtained from swelling data is independent of network imperfection and uniquely represents the network connectivity required for the evaluation of data. The values of the χ parameter at different values of v_2, given in ref 11, show some scatter, due to which eq 5 may not be precise. Reanalysis of this data set by removing the points with high deviation from the mean shows, however, that the error in $\xi kT/V^0$ values calculated on this basis falls within ±10%.

Table I
Results of Equilibrium Swelling Measurements in Toluene and Calculations of the Degree of Cross-Linking

sample	v_2 in toluene	κ	$\xi kT/V^\circ$, N mm^{-2} eq 1	$\xi kT/V^\circ$, N mm^{-2} stoichiometry
1	0.067	10	0.0163	0.0578
2	0.056	12	0.0110	0.0385

Calculation of the Degree of Swelling in Cyclohexane. In this section, the degree of swelling of samples 1 and 2 is calculated by equating eq 1 to zero and using the values of κ and $\xi kT/V^0$ obtained from swelling measurements in toluene. A precise relationship for the the χ parameter is required for adopting this procedure. Critical miscibility experiments of Koningsveld, Kleintjens, and Shultz[7] lead to the following expression for χ:

$$\chi = 0.2035 + 90.65/T + 0.3092v_2 + 0.1554v_2^2 \quad (7)$$

Osmotic pressure measurements of Höcker, Shih, and Flory[3] lead to

$$\chi = 0.2305 + 81.67/T + (-0.018 + 98.01/T)v_2 + (-0.168 + 135.50/T)v_2^2 \quad (8)$$

Equation 8 is obtained by series expansion of the general expression given by Höcker et al[3] for the polystyrene–cyclohexane system. Equation of state variables at 25 °C are used in the evaluation of the coefficients appearing in eq 8.

Substituting eq 7 or 8 into eq 1, together with the values of the elastic parameters for the two networks, leads to the evaluation of v_2 numerically for each given temperature. Results are shown and compared with experimental data in Figure 3. The upper dotted curve in the figure shows results of the calculations obtained by using eq 7 in eq 1 for sample 2. The agreement between theory and experiment observed at higher temperatures becomes poorer as the temperature is lowered. Results for sample 1 exhibited a similar trend and are not shown on the figure for the sake of clarity. The lower and upper dashed lines show results of calculations based on eq 8 for samples 1 and 2, respectively. Apart from the two data points below 20 °C

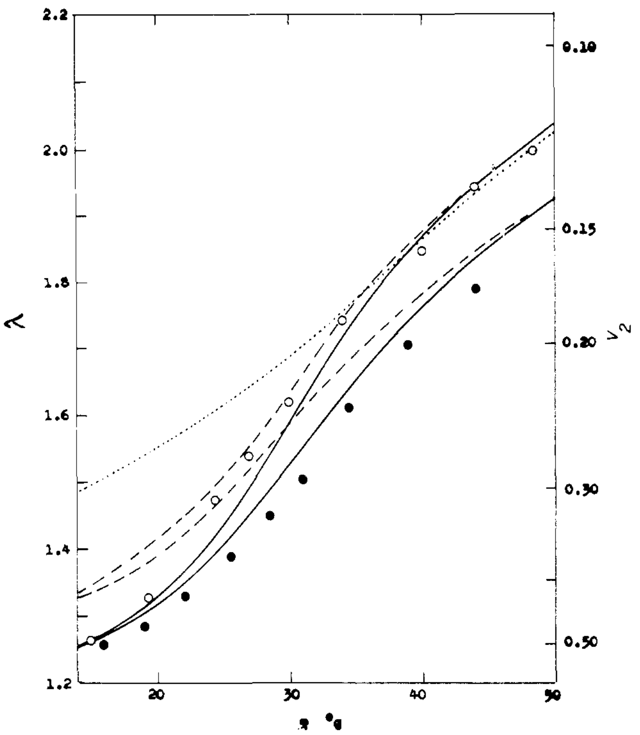

Figure 3. Comparison of predictions of eq 1 with experimental measurements of swelling for polystyrene in cyclohexane. Dotted curve is obtained for sample 1 by using eq 7 for the χ expression. Dashed curves are obtained by using eq 8 as the χ parameter. Lower and upper curves are for samples 1 and 2, respectively. Solid curves are obtained by using eq 8′, the lower curve being for sample 1 and the upper one for sample 2.

for sample 2, calculations and experiments show good agreement. Experimental points for sample 1 fall below the theoretical curve. The maximum discrepancy between theory and experiment, however, is about 6% at 16 °C.

Measurements at low temperature have been taken in both the increasing and decreasing directions, sufficient time being allowed for the system to reach equilibrium. On the basis of the reproducibility of measurements, we conclude that deviations between theory and experiment are real and cannot be attributed to experimental errors. Further examination of eq 1 shows that calculated values of swelling at low temperatures depend very sensitively on the form of the χ parameter used. In order to seek the required modification in the χ parameter for better agreement at low temperatures, a third-order term is appended to eq 8 as

$$\chi = 0.2305 + 81.67/T + (-0.018 + 98.01/T)v_2 + (-0.168 + 135.50/T)v_2^2 + (a/T)v_2^3 \quad (8')$$

Choosing $a = 48.52$ by trial and error leads to the exact agreement of theory with experiment at low temperatures. Theoretical curves obtained with this modified value of χ are shown by solid lines in Figure 3.

The modified values of χ given by eq 8′ for $a = 48.52$ differ by <3% from the value given by eq 8 in the high-v_2 region. For lower concentrations, the difference is <1%. This differences fall well within the experimental error bounds of osmotic pressure determination of the χ parameter, as can be seen from the data of ref 3.

Degree of Swelling of Polystyrene in Toluene–Methanol Mixture and Calculation of the χ Parameter. The linear swelling ratios at different temperatures for sample 1 in toluene–methanol (75/25 wt %) are shown in Figure 2 with empty circles. The best fitting curve through experimental data is represented by the dashed line. The data for swelling of the same sample in cyclohexane are also shown (filled circles) for comparison. Swelling in toluene–methanol appears to depend less strongly on temperature than that observed for cyclohexane. The two curves intersect at about 33 °C, denoting the temperature for which swelling is the same for both systems.

Table II
Experimental Data for the Swelling of Sample 1 in Toluene–Methanol Mixture (75/25 wt %)

temp, °C	λ	v_2	χ^a
15	1.479	0.3091	0.628
25	1.518	0.2859	0.614
30	1.537	0.2754	0.608
35	1.580	0.2535	0.595
40	1.650	0.2226	0.578
44.8	1.689	0.2075	0.569

[a] Calculated from eq 1 with $\xi kT/V^\circ = 0.0163$ N mm^{-2}, $a_1 = 1$, and $\kappa = 10$.

The χ parameter corresponding to each temperature for the polystyrene–toluene–methanol system may be calculated from swelling data and eq 1. Values of χ calculated on this basis are shown in Table II together with results of swelling measurements. Least-squares analysis of the data points gave the following relationship for the dependence of χ on v_2 and T:

$$\chi = 0.4103 + 16.03/T + (0.5054 + 5.60/T)v_2 \quad (9)$$

Due to weaker temperature and concentration dependence exhibited by this system, it was possibile to express the χ parameter without higher order terms in v_2.

Discussion

Agreement of the experimental swelling results of polystyrene in cyclohexane with calculations based on eq 1 directs attention to several features of the theory represented by this equation.

Equation 1 rests on a sensitive balance between the mixing terms given by ln $(1 - v_2) + v_2$, the χ parameter, and the elastic term. Calculations performed but not indicated above show that the replacement of the logarithmic term by the first few terms of its series expansion, as has commonly been done in the past for networks swollen in good solvents, leads to results in total disagreement with experiment. Similarly, the roots, v_2, of eq 1 with $a_1 = 1$ are sensitively dependent on the form of the χ parameter, in particular at lower temperatures where the polymer concentration in the medium is high.

Equation 1 follows from the assumption that the mixing and the elastic free energies are linearly additive. In the past, this postulate of additivity has been tested by measuring the relative activities of solvent in swollen networks and linear chains.[12,13] Interpretation of these experiments showed[14] that they are in support of this postulate of additivity and that supplementary terms in the free energy of mixing are not required. Agreement of swelling results of the present study with calculations based on eq 1 is a further validation of the postulate. Modification of eq 1 by additional terms due to cross-effects between mixing and the elastic energy would lead to swelling ratios in disagreement with those observed in the experiment.

Due to the sensitive dependence of calculated swelling ratios on the χ parameter at higher concentrations, this method seems to be particularly convenient for determinging the interaction parameter of a polymer–solvent system, following the "calibration" of the network with a solvent of known χ parameter. This method has previously been suggested by Orwoll[11] for the evaluation of the χ parameter of polymer–solvent systems.

The polyisobutylene–benzene system may be a suitable candidate for further investigation employing the present experimental technique. The strong dependence of the χ parameter of this system on concentration and temperature has accurately been formulated by previous experiments.[15]

Registry No. (Styrene)·(*p*-divinylbenzene) (copolymer), 9003-70-7; cyclohexane, 110-82-7; toluene, 108-88-3; methanol, 67-56-1.

References and Notes

(1) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, NY, 1953.
(2) Flory, P. J. *J. Am. Chem. Soc.* **1965**, *87*, 1833.
(3) Höcker, H.; Shih, H.; Flory, P. J. *Trans. Faraday Soc.* **1971**, *67*, 2275.
(4) Schick, M. J.; Doty, P.; Zimm, B. H. *J. Am. Chem. Soc.* **1950**, *72*, 530.
(5) Krigbaum, W. R.; Geymer, D. O. *J. Am. Chem. Soc.* **1959**, *81*, 1859.
(6) Scholte, Th. G. *J. Polym. Sci., Part A-2* **1970**, *8*, 841.
(7) Koningsveld, R.; Kleintjens, L. A.; Shultz, A. R. *J. Polym. Sci., Part A-2* **1970**, *8*, 1261.
(8) Brandrup, J.; Immergut, E. H., Eds. "Polymer Handbook"; Interscience: New York, 1967.
(9) Erman, B.; Flory, P. J. *Macromolecules* **1982**, *15*, 806.
(10) Flory, P. J. *J. Chem. Phys.* **1977**, *66*, 5720.
(11) Orwoll, R. A. *Rubber Chem. Technol.* **1977**, *50*, 451.
(12) Gee, G.; Herbert, J. B. M.; Roberts, R. C. *Polymer* **1965**, *6*, 541.
(13) Yen, L. Y.; Eichinger, B. E. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 121.
(14) Flory, P. J. *Macromolecules* **1979**, *12*, 119.
(15) Eichinger, B.; Flory, P. J. *Trans. Faraday Soc.* **1968**, *64*, 2053.

On the Kinetic Theory and Rheology of a Solution of Rigid-Rodlike Macromolecules

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ABSTRACT: A new model is proposed to describe the dynamics of a solution of rigid-rodlike particles. A new expression is obtained for the stress tensor of the solution. The kinetic equation for the problem is solved by using the projection operator method. The loss and storage moduli, non-Newtonian viscosity, and normal stresses are calculated.

1. Introduction

In recent years there has been an increased interest in the study of dynamical and transport properties of nonspherical molecules. In particular, molecules having cylindrical symmetry have been studied extensively due to their importance in the theories of liquid crystals and of linear, rigid polymer particles. The rigid dumbbell and rigid, multibead rod frequently are used as models for these particles. In these models two or more spherical particles or "beads" are spaced at equal intervals along a straight line. The "free space" between the beads is assumed to be penetrable by the molecules of the solvent in which the rodlike particle is suspended. The diffusional (longitudinal transverse) anisotropy of the rod is then a consequence of hydrodynamic interactions among the beads. This "porous rod" model is obviously both inadequate and oversimplified. The large rodlike particles (for example, long polymer chains or cylindrical viruses, like tobacco mosaic virus) more closely resemble continuous impenetrable bodies. Even if some penetration of the "inside" of the polymer particle by solvent is possible, it is unlikely that macroscopic hydrodynamics can be used to analyze the consequences.

In the present paper a new model is proposed for the particle–solvent interaction which we hope will provide a more convenient and realistic tool for the study of rheological properties of such solutions. The mechanical model which we advocate here is that of a continuous, thin fiber, impenetrable to the solvent and characterized by a uniform distribution of the mass along its length (slender body). The spatial configuration of such a particle is described by the location of its center of mass and by a vector directed along the particle axis. The length of this vector is proportional to the length of the particle. For a strictly rigid particle (which we shall consider in this paper) it is only necessary to introduce a unit vector parallel to the long axis of the molecule, since the particle has but five degrees of freedom.

The anisotropic mobility of the particle can be taken into account by assigning to it a cylindrically symmetric friction tensor. The two friction coefficients associated with this tensor can be identified with the familiar expressions of slender-body hydrodynamics[1]

$$\xi_{\parallel} = \eta_0 L \frac{2\pi}{\ln (L/a) - 3/2 + \ln 2} \tag{1.1}$$

and

$$\xi_{\perp} = \eta_0 L \frac{4\pi}{\ln (L/a) - 1/2 + \ln 2} \tag{1.2}$$

Here $\xi_{\parallel}$ and $\xi_{\perp}$ are the friction coefficients for motions in the longitudinal and transverse directions, η_0 is the solvent viscosity, L is the particle length, and a is the cylinder radius. However, we think it is more reasonable to determine the value of these coefficients from experimental data such as, for example, the translational and rotational diffusion constants at infinite dilution. The reason for this is that the macroscopic hydrodynamic theory from which the formulas (1.1) and (1.2) are derived may not adequately account for the drag on an individual molecule and even if it did we do not know what type of boundary conditions should be used. For example, for the tobacco mosaic virus (TMV), which is a very good example of a rigid-rodlike particle, the ratio $\kappa = \xi_{\parallel}/\xi_{\perp}$ of the friction coefficients calculated from the above expressions is about 0.7, while the same ratio calculated from existing experimental data (on translational and rotational diffusion) is about 0.3. The same ratio has been computed by Kirkwood and Auer[2] for

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